

An oscillating C_2^{2-} unit inside a copper rectangle

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Electronic Supplementary Information

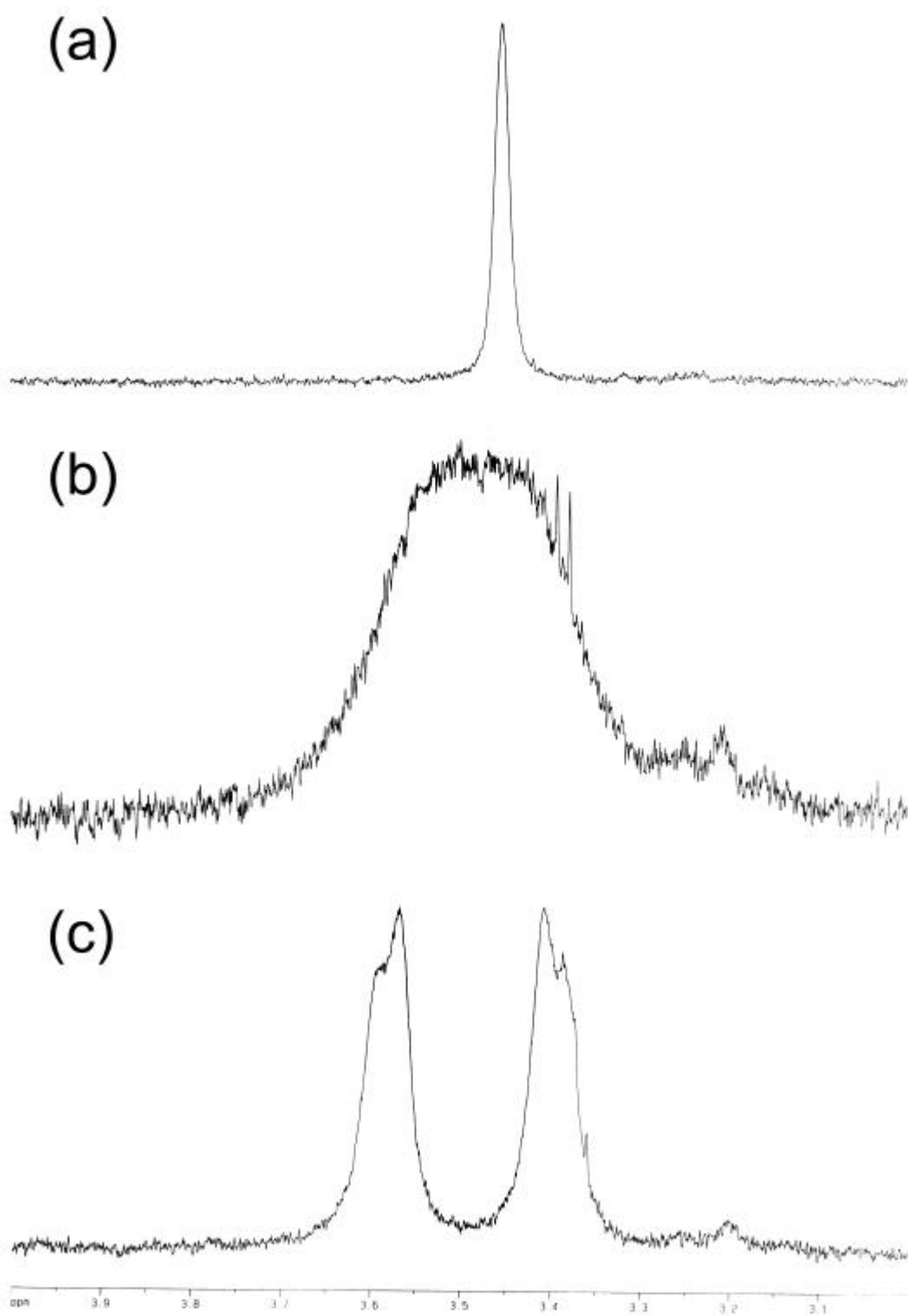
Computational Details

All calculations have been performed with the Gaussian 98 package¹ within the hybrid DFT (Becke3LYP)² level. Two basis sets, I and II, have been used. Basis set I, used for geometry optimizations and frequency calculations, is double- ζ for all atoms (LANL2DZ for Cu and P³; 6-31G for acetylide carbons⁴) except the phosphine substituents which are described with a minimal STO-3G basis.⁵ Basis set I consists of 214 basis functions. Basis set II, which was used to refine the energetics, is double- ζ for all atoms, including the phosphine substituents (6-31G for C, H), and includes polarization functions on phosphorus⁶ and on the acetylide carbons (6-31G(d)).⁷ Basis set II consists of 304 basis functions. The computed free energy values for basis set II were obtained by adding the basis II electronic energy to the thermal, zero-point and entropic corrections computed with basis set I. All calculations were carried out without any symmetry constraint. The nature of all optimized stationary points was confirmed through analytic calculations of the second derivatives.

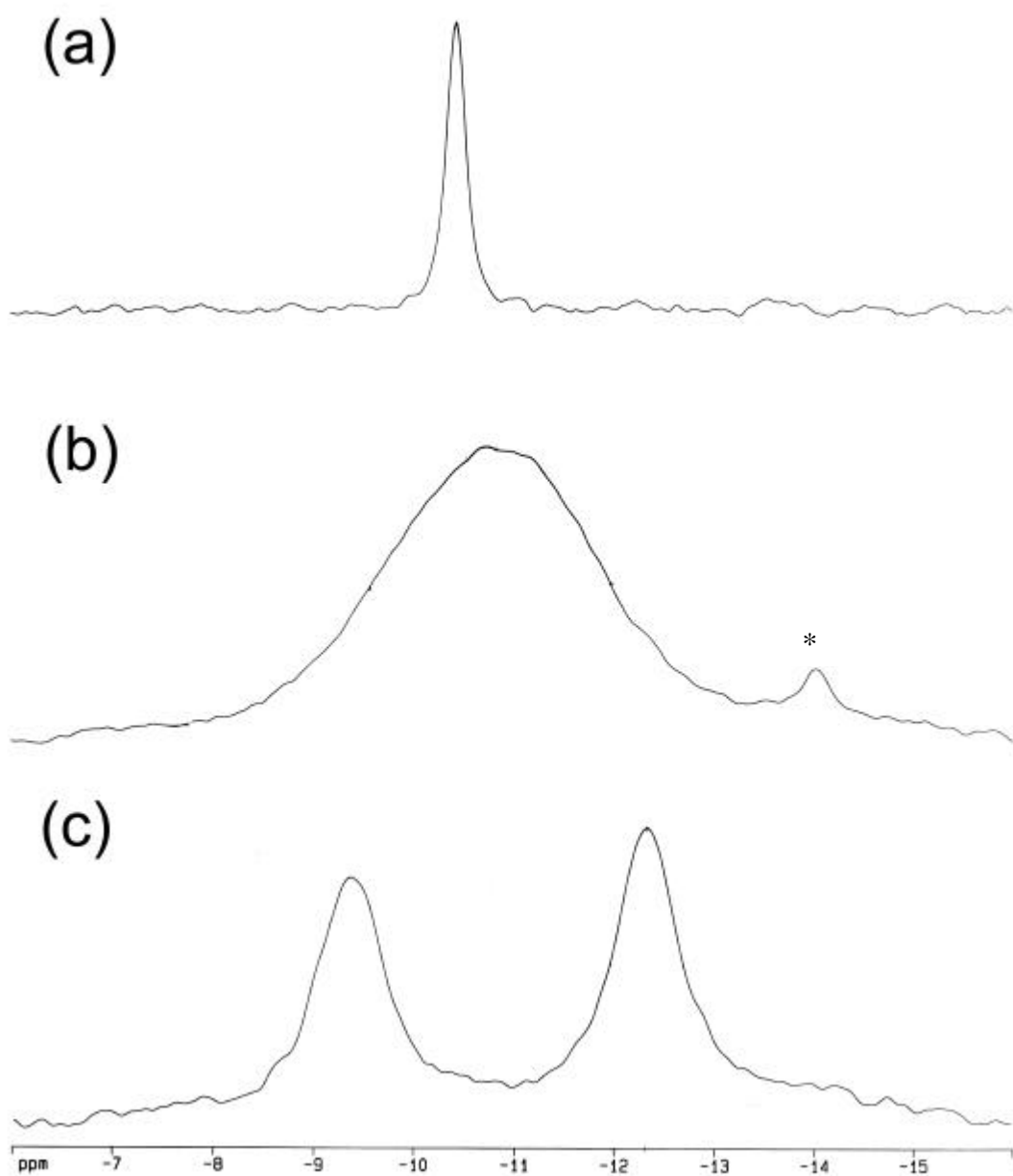
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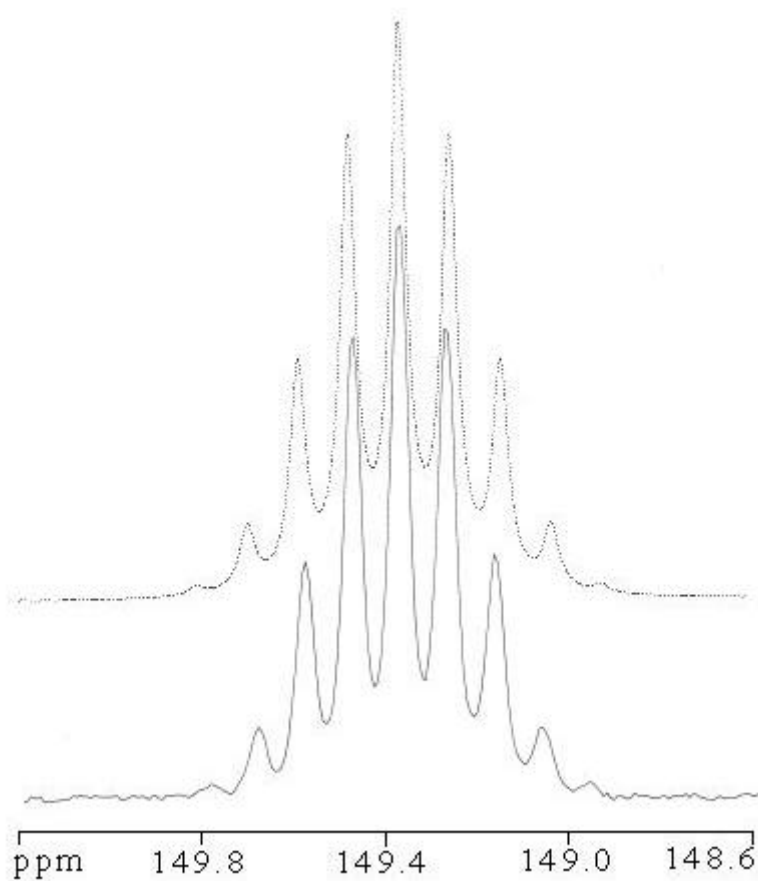
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^1H NMR (500MHz) spectra of $[\text{Cu}_4(\mu\text{-dppm})_4(\mu_4\text{-}\eta^1, \eta^2\text{-}^{13}\text{C}\equiv^{13}\text{C-})]^{2+}$ recorded in dichloromethane- d_2 at (a) 273 K (b) 234 K, and (c) 198 K



$^{31}\text{P}\{^1\text{H}\}$ NMR (202MHz) spectra of $[\text{Cu}_4(\mu\text{-dppm})_4(\mu_4\text{-}\eta^1, \eta^2\text{-}^{13}\text{C}\equiv^{13}\text{C-})]^{2+}$ recorded in dichloromethane- d_2 at (a) 273 K (b) 195 K, and (c) 182 K. (*) is an impurity



The experimental (bottom trace) and simulated (top trace) ^{13}C NMR spectrum of $[\text{Cu}_4(\mu\text{-dppm})_4(\mu_4\text{-}\eta^1, \eta^2\text{-}^{13}\text{C}\equiv^{13}\text{C-})]^{2+}$ recorded in dichloromethane- d_2 at room temperature with 6 hr data accumulation.